PLATING APPARATUS FOR SEMICONDUCTOR WAFER

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Equivalents:

Abstract

PURPOSE:To form a metal as a wiring material on the semiconductor wafer surface by means of an electrolytic plating with a good performance, by providing a distribution correcting plate on the net-like member of an anode electrode opposing to the surface to be plated, and disposing a second positive electrode connected to the positive electrode in plating along the plating unit body.
CONSTITUTION:A reference numeral 21 denotes a plating unit body made of Teflon or the like, while a numeral 22 represents what is called a cathode electrode 22 which serves as the negative electrode in plating. A semiconductor wafer support 22a arranged to contact to the cathode electrode is formed into a needle-like shape under the necessity for supplying a plating current to the surface to be plated. A distribution correcting plate 27 (a disc bored in its center) made of an insulating material such as Teflon is installed on the upper surface of a net-like member 23a of an anode electrode 23. A second positive electrode (auxiliary electrode) 28 connected to the anode electrode 23 (having the same potential as the anode electrode) is installed along the inner wall of the plating unit body 21. A numeral 25 represents a semiconductor wafer having a part to be plated so that a plated wiring will be formed thereon, while a numeral 26 denotes each of arrows showing how a plating solution flows.

Hybrid Polyaryletherketone Membranes for Fuel Cell Applications

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Abstract

Hybrid membranes incorporating an inorganic and organic component are receiving much attention as promising solid electrolytes for fuel cells. Recent developments in the approaches to the preparation of hybrid membranes are described. The preparation and characterisation including their performance in a hydrogen – oxygen fuel cell of two examples of hybrid systems based on sulfonated polyaryl etherketone are described. The examples are chosen to illustrate the formation *in situ* of inorganic particles, either in a pre-formed membrane, or in a polymer solution. sPEEK modified silica and sPEEK-zirconium phosphate membranes provide power densities of 0.62 W/cm² at 100 °C.

1 Introduction

Recent progress in membranes for medium temperature fuel cells includes not only the synthesis of new functionalised proton conducting polymers or their modification by acid- or base-doping, but also associations of polymers (polymer blends), better understanding and control of polymer microstructure, the development of composite systems incorporating a micro- or macro-reinforcement, and hybrid membranes containing an inorganic component in addition to the polymer matrix [1-6].

A number of thermally stable, so-called "advanced" hydrocarbon or heterocyclic polymers are commercially available. The sulfonation of such polymers is an attractive option in the development of new electrolytes for the medium temperature range since it avoids a polymer synthesis step with the associated requirement either of the commercial availability or the preparation of the corresponding monomers. The degree of sulfonation must be carefully controlled however, since the degradation mechanism of such systems seems to be associated with a high concentration of sulfonic acid sites, and highly sulfonated polymers tend to swell excessively in water [1, 6]. The presence of an inorganic proton-conducting component can contribute to the overall conductivity of a composite or hybrid system, such that a polymer of more moderate extent of sulfonation, conductivity, and limited swelling characteristics can be used. Beyond the association of conduction properties of the two components, inclusion or *in situ* formation of inorganic particles can provide other advantages that have been, in recent years, clearly identified by us and others [7]. For example, a homogeneously dispersed hydrophilic inorganic solid assists in improving membrane water management, by improving self-humidification of the membrane at the anode side by enhancing the back-diffusion of water produced at the cathode. This is a key factor for fuel cell functioning with no or low humidification of reactant gases. The presence of finely divided inorganic particles also contributes to inhibiting direct permeation of reaction gases and could participate in limitation of fuel crossover in direct methanol fuel cells (DMFC) [8]. If a specific interaction is favoured between the inorganic and organic components, then improvements in mechanical properties are also to be expected. Since mechanical fragility is one of the principal reasons for membrane failure in long-term *in situ* fuel cell tests [9], development of means of improving mechanical strength will also directly address one of the current bottlenecks to more reliable long-term performance. In a first section this article will briefly review current advances to formation of hybrid and composite inorganic-organic membranes, in particular for medium temperature fuel cells, and will then illustrate developments with two examples using *in situ* growth method for the preparation of hybrid systems based on polyaryletherketones.

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2 Current Approaches to Hybrid Membrane Formation

Routes to the preparation of a membrane system incorporating both inorganic and organic components may be broadly divided into those making use of a pre-formed inorganic solids and those in which the inorganic particulate or network arrangement is formed *in situ* in an organic polymer solution or membrane. On simple dispersion by mixing of a powder form proton conductor into solution of sulfonated polymer [10, 11], non-homogeneous membranes containing rather large particles may result. Indeed, these two factors are two principal criteria in current research on hybrid membrane formation. Size reduction of the inorganic particle will allow greatest contact with the organic component and, since frequently the conduction pathway is across the surface, proton conductivity will tend to increase as the particle size is reduced. Improvement in the dispersion of the inorganic phase through the polymer solution can be obtained if the former can give a stable colloidal suspension in the same solvent, or a solvent miscible with that of the sulfonated polymer.

In situ preparation within the organic phase by precipitation, or hydrolysis and condensation of organometallic precursors in an acid- or base-catalysed sol-gel process, favour intimate combination of the polymer with inorganic precursor monomers and represent an effective alternative to the direct incorporation of a powder-form inorganic material. Two means of polymer *in situ* chemistry have been developed, and the preferred use of one or the other is a function of the nature of the precursor and the properties of the polymer. In a first route, the inorganic phase is formed locally in a pre-formed sulfonated polymer membrane [12–14], and it requires the incorporation by ion-exchange or impregnation/permeation of an appropriate precursor, followed by hydrolysis or precipitation, ageing and drying steps. In the second route, an inorganic alkoxide monomer is added to a solution of the polymer, and hydrolysis and condensation induced by the addition of water and catalyst. An important difference between the membranes obtained concerns the ultimate microstructure, since in the first case, the pre-existing polymer microstructure in the membrane is conserved and inorganic (proton conducting) particles are formed within the confines of the hydrophilic regions. In the second case however, inorganic particles precipitate and ripen at the same time as the polymer microstructure is being reformed and, depending on the interaction between organic and inorganic components, and on the relative amounts of each, a different local morphology may result, which will influence conduction, water retention and mechanical properties.

Polyaryletherketones are thermostable polymers in which ether (E) and ketone (K) units connect phenylene rings giving a range of polymers of the types PEK, PEEK, PEKEKK *etc.* These are insoluble and insulating polymers. Sulfonation in concentrated sulfuric acid [3, 11, 15, 16] occurs more or less readily depending on the composition in E and K units, to give polymers soluble in solvents such as dimethylsulfoxide, dimethyl-

acetamide or N-methylpyrrolidone. The conduction, thermal, and mechanical properties of sPEEK [3, 11, 15], and its fuel cell performance on hydrogen-air and hydrogen-oxygen up to 110 °C [1, 15], as well as in DMFC [5, 17], have been reported in recent years, and long-term tests have claimed lifetimes of up to 4300 h at 50 °C [18]. Sulfonated PEEK is a particularly versatile candidate for preparation of hybrid membranes. The solubility in certain organic liquids referred to above opens up the possibility of an *in situ* sol-gel process in a solution of sPEEK. In addition, the ion exchange properties conferred by the presence of sulfonic acid groups can be used to implant metal ions that act as centres for the local precipitation and growth of inorganic proton conductors. Such routes using sol-gel and ion-exchange processes in general limit particle size to the nanometer scale (nanocomposites) and allow molecular level contact between the inorganic and organic phases. In this context it is important to note a further approach that will not be further expounded below, in which a metal alkoxide solution is permeated through a pre-formed sulfonated polymer membrane, and the corresponding metal oxides particles precipitated *via* hydrolysis and condensation [12].

3 Experimental Procedure

sPEEK was prepared as described previously [15]. Membranes of sPEEK having a cation exchange capacity corresponding to an equivalent weight of *ca.* 770 g/mol were drawn on glass plates and dried in a vacuum oven at 100 °C. The membranes were removed from the glass supports by immersion in a water bath, and were treated with HCl (1 mol/dm^3, 1 h) to ensure presence of the hydrogen form of the membrane, and to remove any traces of organic solvent. Zirconium phosphate was prepared *in situ* by immersing hydrogen form sPEEK membranes in an aqueous solution of ZrOCl$_2$ 8H$_2$O. They were then removed, rinsed with water, and transferred to a vessel containing phosphoric acid (1 mol/dm^3). After heating at 80 °C for 5 h, the membranes were then removed, rinsed with water and conserved in sealed plastic sachets.

Aminophenyltrimethoxysilane and TEOS in mass ratios of 0:100, 10:90; 20:80 and 30:70% in amounts calculated to give hybrid systems with 10, 20 or 30 wt% SiO$_2$ were added to an sPEEK solution in NMP. Following addition of catalytic amounts of HCl, the mixture was heated to 80 °C until a homogeneous solution was formed. Membranes were cast on glass plates, dried and recovered as described above.

Ac conductivity measurements were performed in the range 5 Hz – 13 MHz using an oscillation voltage of 100 mV. Polarisation characterisation were obtained in a single cell of active surface area 5 cm^2. Electrodes were supplied by E-TEK, and were loaded with 1 mg Pt and 0.35 mg Nafion® per square centimetre. The fuel cell was supplied with humidified hydrogen at 3.6 bars absolute pressure, humidification being achieved by bubbling through water held at the same temperature as that of the fuel cell.

4 Zirconium Phosphate – Sulfonated Polyaryletherketone Hybrids

Metal hydrogen phosphates and phosphonates have been extensively studied for their proton conduction properties [19]. They are stable with respect to hydrolysis in an acidic environment, and they represent, probably, the most appropriate inorganic proton electrolytes for low and medium temperature electrochemical applications. In the bulk, metal(IV) hydrogen phosphates [M(IV) = Zr, Sn, Ti...] are synthesised by precipitation from an aqueous solution of M(IV), by reaction with phosphoric acid. In general, the size of the crystallites formed increases with the concentration of phosphoric acid used, the temperature of the reaction medium, and duration of the reaction [20]. Zirconium phosphate of so-called α-structure [α-Zr(HPO₄)₂ H₂O, α-ZrP] can be obtained as a gel and as single crystals, as well as with differing degrees of crystallinity between these limits. α-ZrP can be prepared by heating the amorphous form in concentrated phosphoric acid [20], by direct preparation from a solution of Zr^{4+} in a mixture of phosphoric and hydrofluoric acids [21], or by complexation of zirconium propoxide with phosphoric acid, followed by heating the amorphous material obtained in concentrated phosphoric acid [22]. Crystalline α-ZrP has the layered structure shown in Fig. 1, in which monohydrogen phosphate groups line the upper and lower surfaces of a plane formed by zirconium atoms. The influence of the concentration of phosphoric acid on the crystallinity of the zirconium phosphate obtained was studied using powder X-ray diffraction by Clearfield *et al.* during the 1970 s [20]. These results are of relevance in the present context and Fig. 2 reproduces the X-ray diffraction patterns obtained. In summary, the gel form is obtained for a H_3PO_4 concentration of 0.5 mol/dm³, and the crystalline form with H_3PO_4 12 M. Amorphisation is accompanied by a broadening of the 002 diffraction line. The con-
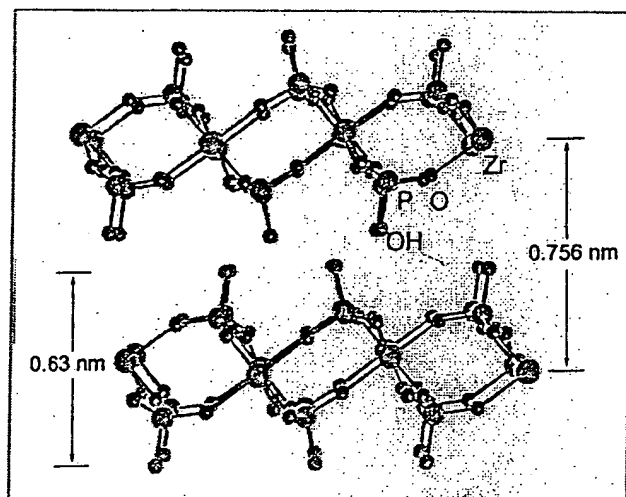
ductivity of α-ZrP is also a function of its crystallinity and particle size. For the amorphous material, the conductivity reaches 10^{-3} S/cm¹ but decreases to 10^{-7} S/cm¹ for the crystalline form. Conductivity increases in an almost linear fashion with relative humidity [19].

It is well-known that the tetranuclear cations $[Zr_4(OH)_8 (H_2O)_{16}]^{8+}$ that make up the structure of solid $ZrOCl_2$ 8H₂O, also persist into solution. Elemental analysis of sPEEK-Zr (membranes recovered after ion-exchange) and sPEEK-ZrP are compatible with the uptake of a condensed species, but in a less highly charged form (average charge per zirconium atom 1 – 2). The experimental conditions described above lead to a hybrid membrane containing 25 wt% of zirconium phosphate, in which the elemental ratio of zirconium to phosphorus is 1 to 2. These data are compatible with the maximum theoretical weight percent of ZrP that can be formed (33 wt%) on the basis of the ion exchange capacity of the sPEEK membrane used. The X-ray diffraction pattern of a hybrid sPEEK-ZrP membrane is compared with those of non-modified sPEEK and with bulk α-ZrP in Fig. 3. sPEEK alone provides only a background signal, while the diffraction lines of bulk α-ZrP are observed also in the pattern of the hybrid membrane sPEEK-ZrP. However, the diffraction line at lowest angle, *ca.* 11.8° 2θ, is only weakly observed. This line corresponds to diffraction from the layers of α-ZrP and the loss in intensity indicates the association of only a limited number of zirconium phosphate layers. An estimate of the particle

Fig. 1 Schematic representation of the structure of α-Zr(HPO₄)₂ H₂O (reproduced with permission from G. Alberti, La Chimica e l'Industria, 1998, p. 608).
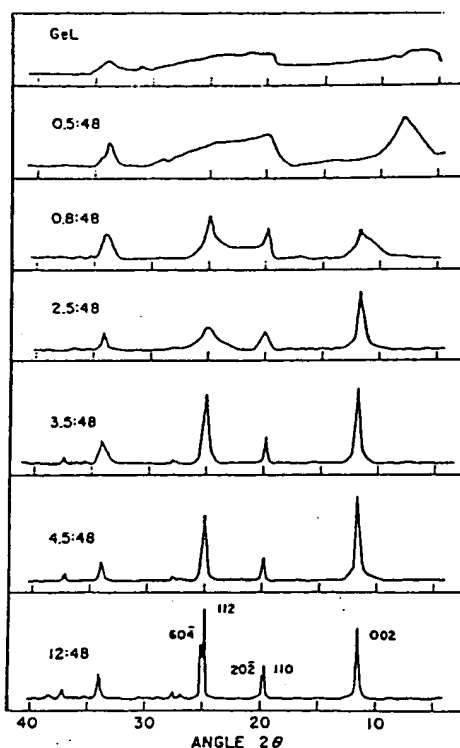

Fig. 2 Evolution of X-ray diffraction patterns of zirconium phosphate with molarity of phosphoric acid and duration of the reaction in hours. Reproduced with permission from Ref. 20.
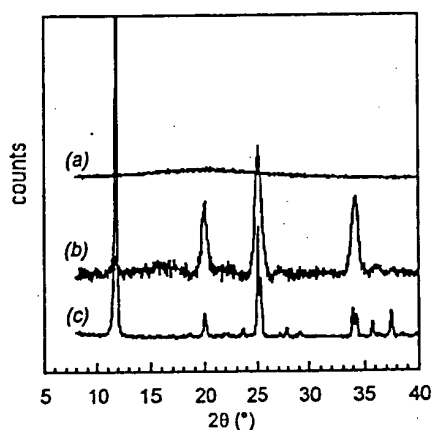
Fig. 3 X-ray diffraction patterns of an sPEEK-zirconium phosphate (ZrP) membrane containing 25 wt% ZrP (b) compared with those given by a pristine sPEEK membrane (a) and bulk α-ZrP (c).
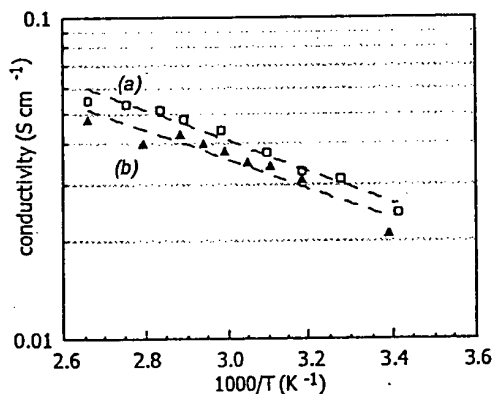

Fig. 4 Conductivity of (a) sPEEK (b) sPEEK-zirconium phosphate (25 wt% ZrP) at 100% RH as a function of reciprocal temperature.
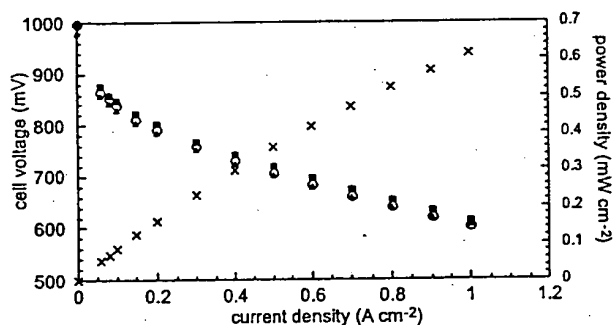

Fig. 5 Polarisation characteristics of an sPEEK-zirconium phosphate (25 wt% ZrP) at 85 °C (O) and 100 °C (■) compared with sPEEK membrane of similar thickness at 85 °C (▲), and power density provided by the hybrid system at 100 °C.

(domain) size can be made from the width of diffraction lines using the Scherrer equation. This provides a value of *ca.* 11 nm. The thickness of a single zirconium phosphate layer is *ca.* 0.65 nm, and it may be concluded that, on average, the particles correspond to 15 – 17 layers. Finally, it is of interest to note that the diffraction pattern given by sPEEK-ZrP is

compatible with that of a bulk sample prepared under similar conditions of phosphoric acid concentration and reaction time. Local characterisation of the phosphorus environment in the hybrid membranes was provided by ^{31}P MAS NMR. In general, the environments $(OH)_2PO_2$, $OHPO_3$ and PO_4 in layered zirconium phosphates occur in the regions *ca.* -9 ppm, -18 ppm and *ca.* -27 ppm respectively [23], although these positions are modified if the hydrogen phosphate groups interact with another species through hydrogen bonding, or if a proton has been transferred [24]. The position of the resonance observed in the NMR spectrum of the hybrid sPEEK-ZrP at -18.8 ppm is in agreement with an environment $OHPO_3$, as expected for α-ZrP.

Electrochemical characterisation of sPEEK-ZrP membranes was carried out using impedance spectroscopy. Following pre-treatment in boiling water for 60 min., membranes, generally of 60 μm thickness, were inserted between the stainless steel electrodes of a closed conductivity cell. This cell enabled the environment to be maintained at 100% relative humidity (RH), and the temperature to be controlled up to 110 °C. The results, reproduced in Fig. 4, show that the conductivity of sPEEK-ZrP containing 25 wt% inorganic component, is only weakly temperature dependent. The conductivity increases from $2 \cdot 10^{-2}$ S/cm to $5 \cdot 10^{-2}$ S/cm between 20 and 100 °C. Further, these values are almost identical to those of the corresponding polymer-only membrane, also shown in Fig. 4, indicating either good percolation in the polymer phase or, most probably, that the inorganic phase participates in proton transfer through the hybrid system.

Similar membranes were mounted without pressing or hot-pressing in a single cell of active surface area 5 cm². Polarisation characteristics on oxygen at 3.6 bars absolute pressure at 85 and 100 °C are shown in Fig. 5, along with the corresponding power density. Under these conditions, this membrane electrode assembly gave about 1 A/cm² at 0.6 V. These results may be compared with those recently reported for a composite Nafion-115-ZrP membrane [25], which provided *ca.* 0.7 A/cm² at 0.6 V, 130 °C and 3 bars pressure, E-TEK electrodes loaded with 0.4 mg/cm².

5 Silica – Sulfonated Polyaryletherketone Hybrids

In recent years a number of polymers (polydimethylsiloxane, polytetramethyleneoxide, polymethylmethacrylate, epoxy resins and polyimides [26]) have been used as host matrix for *in situ* sol-gel polymerisation of silica precursors. Advantages include mechanical properties superior to those of the organic matrix alone. In such hybrid systems, the nature of the interaction between inorganic and organic components depends upon the synthetic approach adopted and two distinct classes, having a covalent bond between components on the one hand and weak hydrogen bonding interactions on the other, have been described [27]. In the realm of sulfonated polymer – silica membranes, the only work in which an *in situ*